Molecular Dynamics Simulation Study on a Monolayer of Half [2]Rotaxane Self-Assembled on Au(111).

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Supporting Information

S1. Force field

We used a force field (FF) based on the Dreiding FF.[1] The functional forms and parameters are given in Tables S1-S2 and Figure S1.

This FF excludes nonbonding interactions between bonded atoms (1,2-pairs) and atoms bonded to a common atom (1,3-pairs). Except for the Au-S pair for which the van der Waals (vdW) parameters were specified explicitly, the off-diagonal van der Waals (vdW) parameters (between different atom types) were determined from the diagonal vdW parameters (between the same atoms types) by the standard combination rule.[1]

For the angle bending term for PF_6, a cosine function (with the periodicity of 4), instead of the usual harmonic function, was used to keep it octahedral.

The torsion term for the O-C(sp^3)-C(sp^3)-O bond in the ethylene oxide linker between TTF and DNP was fit to reproduce the QM (B3LYP/6-31G**) potential energy curve calculated along the torsion scan with respect to the central bond of $CH_3OCH_2CH_2OCH_3$ (Figure S2).

Table S1. Functional forms used in the force field.[a]

$$E = E^{nonbond} + E^{valence}$$

$$E^{nonbond} = E^{coulomb} + E^{vdW}$$

$$E^{valence} = E^{bond} + E^{angle} + E^{torsion} + E^{inversion}$$

$$E_{ij}^{coulomb}(R) = C_0 \frac{q_i q_j}{\varepsilon R_{ij}}$$

$$E_{ij}^{vdW}(R) = D_0 \left\{ \left[\left(\frac{6}{\varsigma - 6} \right) e^{\varsigma \left(1 - \frac{R}{R_0} \right)} \right] - \left[\left(\frac{\varsigma}{\varsigma - 6} \right) \left(\frac{R_0}{R} \right)^6 \right] \right\}$$

$$E^{bond}(R) = \frac{1}{2} K_R (R - R_0)^2$$

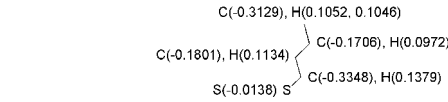
$$E^{angle}(\theta) = \frac{1}{2} \frac{K_\theta}{\sin^2 \theta_0} (\cos\theta - \cos\theta_0)^2$$

$$E_{Oh}^{angle}(\theta) = \frac{1}{2} \frac{K_\theta}{N^2} \left[1 - B(-1)^N \cos(N\theta) \right] \quad (N = 4)$$

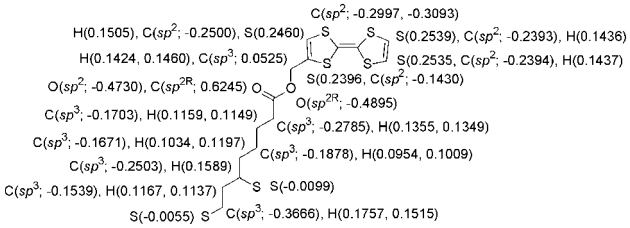
$$E^{torsion}(\varphi) = \frac{1}{2} \sum_n K_{\varphi,n} [1 - d \cos(n\varphi)]$$

$$E^{inversion}(\omega) = \frac{1}{2} \frac{K_\omega}{\sin^2 \omega_0} (\cos\omega - \cos\omega_0)^2$$

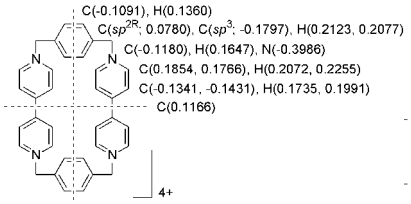
[a] The constants in $E^{Coulomb}$ are the dielectric constant ($\varepsilon = 1$) and C_0 = 332.0637 (the unit conversion factor when atomic charges are in electron units (|e|), the distance R is in Å, and $E^{Coulomb}$ is in kcal/mol).



(a) butanethiolate (BuS?)



(b) thioctate-TTF



(c) $CBPQT^{4+}$ (d) PF_6^-

Figure S1. Atomic charges (q_i) used in the force field. They were calculated quantum mechanically at the B3LYP/6-31G** level on the final geometry of each component optimized separately at the same level of theory using *Jaguar* v4.2. The geometries and charges of BuS? (doublet) and thioctate-TTF (broken S-S; triplet) were calculated using the unrestricted DFT.

Table S2. Force field parameters.

E^{vdW} (diagonal)	R_o[a]	D_o[b]	ζ
Au	2.993	3.0346	12
S	4.03	0.344	12
C(sp^3)	3.8983	0.0951	12
H	3.195	0.016	11.8
C(sp^2), C(sp^{2R})	3.8837	0.0844	12
O(sp^2), O(sp^{2R})	3.4046	0.0957	13.483
N(sp^2), N(sp^{2R})	3.6621	0.0774	13.843
P	4.15	0.32	12
F	3.3825	0.05092	15
E^{vdW} (off-diagonal)	R_o[a]	D_o[b]	ζ
Au-S	2.879	4.2048	12
E^{bond}	R_o[a]	K_b[c]	

S-C(sp^3)	1.8	700	
C(sp^3)-C(sp^3)	1.53	700	
C(sp^3)-H	1.09	700	
S-C(sp^2)	1.7	700	
C(sp^2)-C(sp^2)	1.33	1400	
C(sp^3)-C(sp^2)	1.43	700	
C(sp^3)-C(sp^{2R})	1.46	700	
O(sp^2)-C(sp^{2R})	1.25	1400	
O(sp^{2R})-C(sp^{2R})	1.35	1050	
C(sp^{2R})-H	1.02	700	
C(sp^{2R})-C(sp^{2R})	1.39	1050	
N(sp^{2R})-C(sp^{2R})	1.34	1050	
N(sp^{2R})-C(sp^3)	1.41	700	
P-F	1.6378	474.326	
E^{angle}	θ_o[d]	K_θ[b]	
X-C(sp^3)-X	109.47	100	
X-C($sp^{2,2R}$)-X	120	100	
X-S-X	109.47	350	
X-O(sp^{2R})-X	120	100	
X-N(sp^{2R})-X	120	100	
$E^{angle}(O_h)$	N	K_θ[b]	B
F-P-F (in PF_6^-)	4	132.241	+1
$E^{torsion}$	n	K_φ[b]	d
X-C(sp^3)-C(sp^3)-X	3	2.0	−1
O-C(sp^3)-C(sp^3)-O	1	25.5	+1
	2	16.5	−1
	3	9.75	+1
X-C(sp^2)-C(sp^3)-X	3	2.0	−1
O(sp^2)-C(sp^2)-C(sp^3)-X	6	1.0	+1
C(sp^2)-O(sp^2)-C(sp^3)-X	6	1.0	+1
X-C(sp^2)-C(sp^2)-X	2	45.0	+1
X-C(sp^{2R})-C(sp^{2R})-X	2	25.0	+1
X-O(sp^2)-C(sp^2)-X	2	25.0	+1
X-O(sp^2)-C(sp^3)-X	3	2.0	−1
X-N(sp^2)-C(sp^3)-X	3	2.0	−1
X-N(sp^2)-C(sp^2)-X	2	25.0	+1
$E^{invesion}$	ω_o[d]	K_ω[b]	
C($sp^{2,2R}$)-X-X-X	0.0	40.0	
N($sp^{2,2R}$)-X-X-X	0.0	40.0	

[a]In Å. [b]In kcal/mol. [c]In kcal/mol/Å^2. [d]In ?.

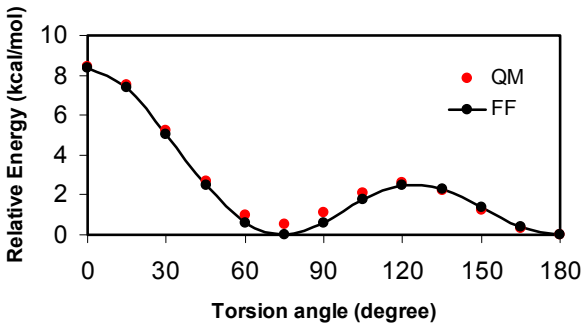
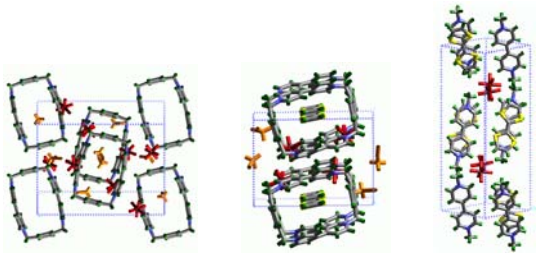


Figure S2. Torsional potential energy curve (QM versus FF) with respect to the central bond of $CH_3OCH_2CH_2OCH_3$.

S2. Force field validation

This set of FF turned out to be very good (Δ < 5 %) in reproducing the density of relevant crystals containing $CBPQT^{4+}$ (or PQT^{2+}, a fraction of CBPQT), PF_6^-, TTF, and/or CH_3CN units (Figure S3) from the 1-ns NPT MD simulation at corresponding temperatures (Table S3).



(a) **VAFRID** (b) **VOLMEO** (c) **UBULUY**

Figure S3. Crystals of CBPQT (PQT), PF_6, TTF, and CH_3CN.[2-5]

Table S3. Crystal structure data. Exeriment[2-5] versus calculation.

	Code	Contents	T /K	ρ_{expt}	ρ_{MD} (Δ)
(a)	VAFRID	CBPQT, PF_6, CH_3CN	293	1.500 g/cm^3	1.432 (4.7%)
(b)	VOLMEO	CBPQT, PF_6, TTF, CH_3CN	295	1.546 g/cm^3	1.594 (3%)
(c)	UBULUY	PQT, PF_6, TTF,	160	1.789 g/cm^3	1.801 (0.67%)

The MD simulation at 298 K using our set of FF gives the binding energy of ~3 kcal/mol between $(CBPQT)(PF_6)_4$ and TTF, which is in the range of the experimental estimates for the free energy of complexation of $(TTF)(CBPQT)(PF_6)_4$ complex (5.3–5.5 kcal/mol).[6-8]

S3. Scheme-dependence

Even though long MD simulations of 1 ns were employed to estimate the coverage-dependence of packing energy in order to ensure enough equilibration and sampling (Figure 4 and Figure S4c), shorter MD simulations (such as 100 ps) or even the minimization only give the same trend of the results (Figure S4).

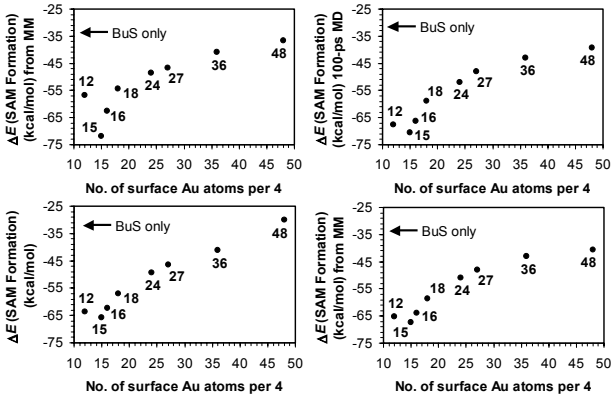


Figure S4. Coverage-dependent packing energy of **4** (a) from the initial minimizations, (b) from shorter (100-ps) NVT MD simulations at 298 K, (c) from longer (1-ns) simulations, and (d) from the final minimizations after the 1-ns simulation (300 ps for the **1**/**48** case).

References

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